

# Influence of Hydrodynamic Interactions on the Kinetics of Colloidal Particle's adsorption

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The kinetics of irreversible adsorption of spherical particles onto a flat surface is theoretically studied. Previous models, in which hydrodynamic interactions were disregarded, predicted a power-law behavior  $t^{-2/3}$  for the time dependence of the coverage of the surface near saturation. Experiments, however, are in agreement with a power-law behavior of the form  $t^{-1/2}$ . We outline that, when hydrodynamic interactions are considered, the asymptotic behavior is found to be compatible with the experimental results in a wide region near saturation.

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The adsorption of colloidal particles or macromolecules such as proteins onto adsorbing surfaces is a very common phenomenon in many fields of Biology, Chemistry and Physics. Deposition of bacteria on teeth or the adsorption of antibodies on living cells are examples of such phenomena which are of great interest in medical sciences. In many cases, the adsorption is irreversible under conditions of practical interest. A model system to study the adsorption process is a suspension of latex spheres put in contact with a suitable adsorbing flat surface. Much work has been done for this system [1–5,7–14], both on the structural properties of the adsorbed layer and on the kinetics of the process. For irreversible adsorption of sufficiently light spherical particles onto a flat surface, Schaaf *et al.* [7] predicted a power-law behavior  $t^{-2/3}$  for the time-dependence of the coverage of the surface near saturation. This behavior is due to the interplay of the diffusion of particles from the bulk and the *blocking effect* caused by the saturation of the surface due to the previously adsorbed particles. This result agrees with Brownian dynamics simulation of spheres diffusing from a bulk solution with a constant diffusion coefficient [16]. Experiments on the adsorption kinetics of small spherical particles (proteins or small latex particles), however, show a power law behavior of the form  $t^{-1/2}$  [15,25] when gravitational effects on the particles can be ignored in front of its pure diffusion. Such a behavior is predicted by kinetic models based on the Random Sequential Adsorption (RSA) filling rules [5]. RSA, however, ignores the physical mechanisms driving the particles to the surface. Thus, it seems that an important physical ingredient has been missed in previous approaches [7]. In this Letter, we will show that hydrodynamic interactions between the particles and the surface substantially modify the predicted asymptotic behavior of the system near saturation. A simple theoretical model taking into account

the blocking effect, the diffusion of the particles from the bulk and the hydrodynamic interactions between the particles and the surface, allows us to predict a complex asymptotic behavior for the time-dependence of the surface coverage near saturation. Indeed, near saturation, the model predicts a wide first time-domain where the time-dependence of the coverage is dominated by the hydrodynamic interactions between the free particles and the adsorbing surface. Remarkably, the time-dependence in this region is compatible with the experimental findings of refs. [15,25]. Furthermore, our model also allows to derive a second time-domain in which the dynamics is dominated by the blocking effect. In this terminal regime, the asymptotic time-dependence of the coverage is in agreement with the predictions of Schaaf *et al.* [7]. Nevertheless, we will see that this terminal regime should not be observed for short-range adsorption potentials, whose interaction range is much smaller than the size of the colloidal particles.

Despite their apparent simplicity, the deposition processes are determined by the interplay of various phenomena: the Brownian motion of the free particles, the gravitational force, the dynamic interactions mediated by the solvent (hydrodynamic interactions) and all other kinds of interactions between free particles and the adsorbed ones, as well as between the free particles and the wall. Irreversible adsorption leads to non-equilibrium configurations, thus, it cannot be studied in the framework of equilibrium statistical mechanics. Most of the previous models [1,5,17,18] have neglected the effect of the solvent. They consider the particles as moving in dry water [19] and have focused primarily on the geometric aspects, related to the excluded surface effects. Recently, however, the determinant role played by the hydrodynamic behavior of the solvent was pointed out [20,21]. For instance, the

theoretically predicted pair distribution function of the adsorbed layer shows significant deviations from the experimental curves for this function when hydrodynamic interactions are ignored [9,10,21,22,28]. The effect of the hydrodynamic interaction is to increase the frictional force experienced by a particle when it approaches a flat surface. Despite its clear implication in the kinetics of the adsorption process, the effect of the hydrodynamic interaction in the time- dependence of the coverage near saturation has never been analyzed before. In the analysis proposed here we assume that the free particles diffusing from the bulk have to cross an *entropic* barrier, due to the presence of the previously adsorbed (bound) particles in the layer, before they get trapped by an adsorbing short range potential between the particles and the plane. The density  $\rho$  of free particles in the region near the wall is assumed to satisfy a diffusion equation of the form [23]

$$\frac{\partial}{\partial t}\rho = -\frac{\partial}{\partial \gamma}J(\gamma, t) = \frac{\partial}{\partial \gamma}\frac{D(\gamma, \theta)}{R^2}\left[\frac{\partial}{\partial \gamma}\rho - \rho\frac{\partial}{\partial \gamma}\ln\Phi(\gamma, \theta)\right] \quad (1)$$

where  $\gamma \equiv z/2R$  is the dimensionless coordinate in the  $z$ -direction orthogonal to the wall,  $R$  being the radius of the particles. The origin of coordinates is taken at the center of an adsorbed particle. In this equation,  $J(\gamma, t)$  is the flux of free particles in the vicinity of the wall. Thus, it is in the region  $0 \leq \gamma \leq 1$  that the effect of the excluded surface due to the presence of adsorbed particles takes place.  $\Phi(\gamma, \theta)$  is the available area for a free particle to move in at a height  $\gamma$  and at a coverage  $\theta$  of the surface [24].  $\theta$  is defined as  $\theta \equiv \pi R^2 \rho_s$ , where the number of adsorbed particles per unit of area is denoted by  $\rho_s$ . The diffusion coefficient  $D(\gamma, \theta)$  is related to the mobility of the free particles. Far from the wall, the diffusion coefficient of spheres in a dilute solution is given simply by the Stokes-Einstein formula  $D = kT/6\pi\eta R$ ,  $\eta$  being the viscosity of the solvent and is constant. Near the wall, however, hydrodynamic interactions modify this behavior. Lubrication theory [27] shows that the mobility in the direction orthogonal to the wall vanishes *linearly* with the distance between the hydrodynamic surfaces. Thus, the diffusion coefficient behaves as

$$D(\gamma, \theta) = (\gamma + \delta)D_0 \quad (2)$$

as  $\gamma \rightarrow 0$ .  $D_0$  is a constant and  $\delta \equiv d/2R$ , where  $d$  stands for the repulsive range of the adsorption potential (fig. 1). Note that the *hydrodynamic* wall is then shifted with respect to the *adsorbing* wall due to the finite range of the adsorption potential considered here.  $\delta$  is finite but can be made arbitrarily small in our model, in order to compare with previous analysis [7]. If  $\delta \rightarrow 0$  no particles can be adsorbed in a finite time due to the strength

of the lubrication forces. The hydrodynamic interaction between the free particles and the adsorbed ones is subdominant for the motion in the direction orthogonal to the wall [27], due to the fact that their surfaces move parallel to each other when  $\gamma \rightarrow 0$ . As a consequence, the diffusion coefficient is independent of the coverage  $\theta$  in this limit.

The diffusion equation (1) contains all the relevant phenomena driving the kinetics of particle adsorption. In the expression between brackets, the first term stands for pure diffusion of the free particles while the second accounts for the fact that the available area at a given height  $\gamma$  and at a given coverage  $\theta$  is limited by the presence of the adsorbed particles. Therefore, if the available area is reduced as  $\gamma$  decreases, this term acts as an effective entropic potential tending to decrease the flux of free particles. Our model can be applied to a large class of systems provided that they meet the following requirements; (i) the particles are irreversibly adsorbed on the surface and stop moving once trapped; (ii) diffusion dominates over gravitational effects in the dynamics of the free particles.

Notice that, the use of equation (1) implies that we describe the transport of the free particles across the layer of adsorbed ones without explicit calculation of the structural properties of the layer. Brownian motion permits the particles to explore large regions in space before they get adsorbed. Thus, one expects that the overall adsorption process is not determined by the local inhomogeneities of the layer of adsorbed particles but by its global properties, in the spirit of a mean field approach [23].

The saturation coverage  $\theta_\infty$ , or *jamming limit*, is reached when on the adsorbing surface ( $\gamma = 0$ ), the available surface function becomes equal to zero. For  $\theta = \theta_\infty$ , the entropic barrier becomes infinite, thus the adsorption of new incoming particles is impossible. For spherical particles, the entropic potential near saturation can be written as

$$\ln\Phi(\theta, \gamma) \simeq \ln(\theta_\infty - \theta(1 - \gamma^2))^3 \quad (3)$$

The form  $(\theta_\infty - \theta)^3$  is the behavior of the available area near saturation for irreversible adsorption of particles, and has been first derived by Pomeau [26]. In addition, we have explicitly indicated the fact that, at a given height, the area excluded by the adsorbed spherical particles is reduced by a factor  $(1 - \gamma^2)$  for spheres [23].

In order to describe the kinetics of the adsorption process, we have to find the incoming flux of free particles arriving at the adsorbing surface  $J_s(t) = J(\gamma = 0, t)$ . Since we are interested only in the kinetics near saturation, where the adsorption process is very slow due to

the blocking effect, we can solve eq. (1) neglecting the explicit time-dependence of  $\rho$ . We then assume that the variations in the density profile and, thus, in the flux, adiabatically follow the changes in the coverage through  $\Phi(\theta, \gamma)$  [23]. Therefore, we set  $\partial\rho/\partial t \simeq 0$  in the left hand side of eq. (1), implying that  $J(\gamma, t)$  is independent of  $\gamma$  and equal in fact to  $J_s(t)$ . We consider here that the density of particles in the bulk  $\rho_B$  is the control parameter and thus express  $J_s$  in terms of  $\rho_B$ , with the boundary conditions

$$\rho(\gamma = 1) = \rho_B, \quad (4)$$

$$\rho(\gamma = 0) = 0 \quad (5)$$

The first boundary condition assumes that the density of bulk particles in the vicinity of the adsorbed layer is approximately constant due to the slow adsorption process occurring near saturation. We thus consider a particle's reservoir located at  $\gamma = 1$  with a density  $\rho = \rho_B$  constant. The second boundary condition stands for an irreversible adsorption: free particles reaching the wall become irreversibly adsorbed and then the density of free particles is zero at  $\gamma = 0$ . We can thus obtain the flux of particles reaching the surface in terms of  $\rho_B$  by solving the differential equation

$$J_s = -\frac{D(\gamma)}{R^2} \left[ \frac{\partial}{\partial \gamma} \rho - \rho \frac{\partial}{\partial \gamma} \ln \Phi \right] \quad (6)$$

with boundary conditions specified in eqs. (4) and (5). We find the following kinetic equation

$$\frac{\partial \rho_s}{\partial t} = -J_s = -\frac{D_0}{R^2} \rho_B I(\theta) \quad (7)$$

where

$$I(\theta) = \frac{1}{\int_0^1 \frac{D_0}{D(\gamma)\Phi(\theta, \gamma)} d\gamma} \sim \frac{1}{\int_0^1 \frac{D_0}{D(\gamma)(\theta_\infty - \theta(1-\gamma^2))^3} d\gamma} \quad (8)$$

as  $\theta \rightarrow \theta_\infty$ . A closed equation for the time-dependence of the coverage then follows by multiplying both sides by  $\pi R^2$ , yielding a generalized Langmuir equation [23]

$$\frac{\partial \theta}{\partial t} = K_a \rho_B I(\theta) \quad (9)$$

where we have defined the kinetic coefficient  $K_a = D_0 \pi$ . A crucial point in our analysis is that the leading contribution to  $I(\theta)$  near saturation depends on the behavior of the integrand for small  $\gamma$ , which allows us to use the expression of  $D(\gamma)$  given in eq. (2). Inserting this dependence in the right hand side of eq. (8) we obtain that the adsorption rate near saturation is proportional to

$$I(\theta) \sim \frac{1}{\int_0^1 \frac{1}{(\gamma+\delta)(\theta_\infty - \theta(1-\gamma^2))^3} d\gamma} \quad (10)$$

The asymptotics of  $I(\theta)$  as given by this expression strongly depends on the relative magnitude of  $\delta$  and  $\Delta\theta \equiv (\theta_\infty - \theta)/\theta_\infty$ . Clearly, when the coverage approaches saturation, in an initial regime the condition  $(\theta_\infty - \theta)/\theta_\infty \gg \delta$  is satisfied since  $\delta$  is a constant that can be taken as arbitrarily small. In this region, the adsorption rate is dominated by the hydrodynamic interactions and takes the asymptotic form

$$I(\theta) \sim \frac{2\Delta\theta^3}{\ln \Delta\theta/\delta^2 - 3/2}. \quad (11)$$

The range of validity of this regime is determined by the fact that  $I(\theta)$  must be positive since eq. (9) describes a relaxation process in which the coverage tends irreversibly to saturation. Effectively, the condition  $\ln \Delta\theta/\delta^2 - 3/2 > 0$  indicates that  $\Delta\theta/\delta^2 > \exp(3/2) \sim 1$ . Therefore, the crossover coverage scales as,  $\Delta\theta_c \sim \delta^2$ . In this region, the time-dependence of the coverage can be obtained by inserting the asymptotic behavior given in eq. (11) in the right hand side of eq. (9). After integration we obtain

$$t \sim \frac{\ln \Delta\theta/\delta^2 - 1}{4\Delta\theta^2}. \quad (12)$$

for  $\Delta\theta/\delta^2 > \exp(3/2)$ . Eq. (12) gives an implicit relation between the time and  $\Delta\theta$ . The scaling of the crossover time  $t_c$  is obtained by inserting the scaling of the crossover coverage in this expression, giving  $t_c \sim 1/\delta^4$ . Notice the fact that if  $\delta \rightarrow 0$ ,  $t_c \rightarrow \infty$ , indicating that this regime must dominate the asymptotic behavior of the coverage near saturation. The numerator on the right hand side of eq. (12) is a slowly varying function of  $\Delta\theta$ . This suggests an iterative procedure to obtain the behavior of  $\Delta\theta$  for times  $t \ll t_c$ . Effectively, one can write

$$\Delta\theta \sim \frac{1}{2t^{1/2}} \sqrt{\ln \left( \frac{\Delta\theta}{\delta^2} \right)} \sim \frac{1}{2t^{1/2}} \sqrt{\ln \left( \frac{1}{2\delta^2 t} \right)} \quad (13)$$

where, in deriving the last expression, a term  $\sqrt{\ln \ln(\Delta\theta/\delta^2)} \sim 1 \ll \ln(1/2\delta^2 t)$  has been neglected. Eq. (13) predicts a novel behavior for the time-dependence of the coverage near saturation dominated by the hydrodynamic interactions between the free particles and the wall. Such a behavior differs from that found from the RSA model [6] as well as from that predicted by the model incorporating the diffusion of the particles from the bulk [7].

The terminal regime  $t \gg t_c$  or, equivalently,  $\Delta\theta/\delta^2 < 1$  can also be obtained from eq. (10). The adsorption rate

in this case is dominated by the blocking effect and obeys a different asymptotics of the form

$$I(\theta) \sim \delta (\theta_\infty - \theta)^{5/2} \quad (14)$$

Notice that the right hand side of this equation vanishes as  $\delta \rightarrow 0$ . From eq. (9) and (14) one arrives at the  $\Delta\theta \sim t^{-2/3}$  behavior as found by Schaaf *et al.* [7]. Therefore, the model proposed here is also able to reproduce Schaaf's regime [7] when the adsorption kinetics is dominated by the blocking effect. However, due to the fact that the crossover time between the two regimes scales as  $\delta^{-4}$  and tends to infinity as  $\delta \rightarrow 0$ , it suggests that this regime is never observed for short range adsorption potentials.

In summary, we have explicitly discussed a model where the hydrodynamic interactions are included, in addition to other physical mechanisms like diffusion and blocking effect, which are relevant to describe the adsorbing rate. Hydrodynamic interactions play a crucial role in the adsorption kinetics and cannot be avoided in any experimental work on this process. Previous models ignore the physical mechanisms driving the particles to the surface (see ref. [5] and related). Schaaf *et al.* [7], by taking into account the diffusion of the particles from the bulk as well as the blocking effect, made a significant step in the description of adsorption kinetics. However, the behavior predicted by Schaaf *et al.* has never been observed. Experimental results [15,25] suggest a behavior near saturation compatible with a power law  $\Delta\theta \sim t^{-1/2}$ . An important conclusion that can be drawn from the present work is that the regime predicted by Schaaf *et al.* should not be observed for short range adsorption potential. The most relevant result of this Letter is, however, to have shown that the inclusion of hydrodynamic interactions leads to a behavior near saturation compatible with the experimental findings, in view of the slow behavior of the logarithmic factor in eq. (13). As it has already been pointed out for structural aspects of colloidal particles' adsorption onto solid surfaces [20,21], the results of the present work stress the importance of the hydrodynamic interactions also in the kinetics of the process.

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## FIGURE CAPTIONS

Schematic representation of the adsorption process. The adsorbing (free) particles diffuse in the bulk and get finally adsorbed at a distance  $d$  (arbitrarily small) from

the wall. The origin of the dimensionless coordinate  $\gamma$  is taken in the plane defined by the centers of the adsorbed particles.

